

I. INTERACTION OF THE CONSTITUENTS OF VEGETABLE TANNING EXTRACTS WITH CHROMIUM

ABSTRACT

It has been suggested that the poor resistance of combination chrome-vegetable-tanned leathers to moist heat is due to displacement of sulfate and protein carboxyl groups from the chromium complex by the nontans, and possibly the tans, of the vegetable tanning extracts. The interaction of chromium with such extracts has, therefore, been examined.

Tannic acid and vegetable tans can be almost completely precipitated by chromium salts at pH values above 4.0. Changes in absorption spectra on heating indicate that interaction also occurs at lower pH values but give little information on the extent to which this occurs.

Complexes containing tan and chromium were separated by column chromatography on Solka floc from solutions of chromic sulfate heated with tannic acid or catechol.

Paper chromatography, however, gave little evidence of interaction between chromium and any of the compounds tested but showed clearly that the presence of chromium greatly accentuated the changes taking place in the tan constituents on heating. Uptake of oxygen was also increased, and it is concluded that chromium accelerates oxidation of the tan.

On the basis of the observations reported, it is concluded that interaction occurs between chromium and both the nontans and tans of vegetable tanning extracts. This interaction increases with pH, and with the three tanning extracts tested, it increases in the order: sulfited quebracho, mimosa, myrobalans.

The implications of these findings are discussed, and it is suggested that sulfited quebracho is the most suitable tanning material for use in conjunction with chromium tannages.

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In view of these observations it was considered desirable to obtain further information on the interaction of the constituents of vegetable tanning extracts with chromium and to determine, if possible, the probable optimum ratio of vegetable tannin to chromium for maximum stability to moist heat and perspiration and to indicate which vegetable tanning material is likely to be the most satisfactory for retannage.

Various methods have been used in attempts to obtain such information:

- (1) precipitation of vegetable tans by chromium salts
- (2) examination of the properties of solutions obtained by the addition of chromium salts to vegetable tanning extracts by
 - (a) spectrophotometric methods
 - (b) chromatographic techniques
- (3) studies on the displacement of sulfate ions from the chromium complex by vegetable tanning solutions using isotopic exchange methods
- (4) examination of the factors affecting the extraction of chromium from leather by vegetable tanning extracts

The present paper deals with the work carried out on the properties of vegetable tan-chromium salt solutions under the first two headings above and also with the effect of chromium on the absorption of oxygen by vegetable tanning solutions. The results of experiments on the displacement of sulfate and chromium from leathers by vegetable tanning solutions are described in a subsequent paper.

EXPERIMENTAL

Materials.—Catechol, pyrogallol, resorcinol, and tannic acid were obtained as dry powders from British Drug Houses. Myrobalans, mimosa, and lightly sulfited quebracho solutions were made up from commercial spray-dried powders or extracts.

Chromic nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$) and sulfate ($\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$) were laboratory reagents.

Spectrophotometric measurements.—Solutions of chromic nitrate or sulfate were heated with solutions of the various compounds either under reflux or in stoppered bottles in an incubator at 100°C . To minimize complications due to precipitation the solutions were all adjusted to pH 2.0 before mixing. After heating, the solutions were cooled and filtered if necessary, and the optical density was measured at appropriate dilutions in 1-cm. cells, using a Uvispek Photoelectric Spectrophotometer.

Chromatography.—Paper chromatograms were run on $10'' \times 10''$ Whatman 3MM or No. 2 paper. Phenol components were stained by dipping in 3% ferric chloride–3% potassium ferricyanide followed by washing in dilute hydrochloric acid and water (13).

INTRODUCTION

Previous work has shown that leathers containing vegetable tan and chromium are more susceptible to deterioration under warm moist conditions than leathers tanned with either of these materials alone (1, 2, 3). On the other hand, combination-tanned leathers are generally considered to be more durable in wear (4, 5).

One of the most probable reasons for the poor resistance of semichrome and chrome retan leathers to moist heat is the increase in acidity resulting from displacement of anions from the chrome complex by the nontan acid anions and possibly by the tanning molecules themselves (1, 6, 7, 8). In support of this view the acidity of combination-tanned leather has been shown to increase during storage (1, 2, 6, 7, 9), though this effect is often masked by the uptake of acid by the hydrolyzed protein. Further, Amos, Thompson, and Tolliday (8) have shown that sulfate continues to be slowly displaced when mimosa-tanned leather is stored damp. These authors also show that the mimosa tannin itself, as distinct from the nontans, displaces sulfate in spite of its nonionic character (8, 10).

Loss of chromium on prolonged retannage with vegetable tans (see Gustavson [11], and the fall in shrinkage temperature of most combination-tanned leathers on exposure to warm moist conditions (1, 2, 3) suggest that the nontans and tans in leather may also displace protein carboxyl groups from the chromium complex, thus causing detannage. It is possible that this fall in shrinkage temperature is partially due to the increased acidity and displacement of chromium by hydrogen ions, but since falls also occur with combination leathers adjusted to pH values of 5.0 and above (3), it cannot be the only cause.

If increased acidity due to displacement of sulfate ions from the chromium complex is the primary cause of the deterioration of vegetable-chrome combination-tanned leathers, then masked tannages as suggested by Williams-Wynne and Sykes (6, 7) should be advantageous. If, however, displacement of carboxyl groups is the more important factor, then the presence of strongly complexing organic acid anions may only add to the trouble. Further, in wear the increased acidity may in fact be an advantage, since it will compensate for the rise in pH due to the absorption of perspiration and hence reduce the oxidation of vegetable tan and the darkening and crackiness which accompany it. This could be one of the reasons for the relatively good resistance of combination-tanned leather in wear (4, 5). Another possible reason is that vegetable retannage reduces the detanning action of lactates (12). If the vegetable tan itself displaces chromium, then presumably, there is a maximum value for the ratio of vegetable tan to chromium for optimum stability above which the detanning action will be greater than the protective action against perspiration.

Gradual addition of more alkali led to almost complete precipitation of all four tans. With tannic acid this occurred at final pH values of 3.5 and above and ratios of Cr/tan of 4 or more; with myrobalans, the most readily precipitated, at pH values as low as 2.5 and ratios of 2 or above; with mimosa, at pH values above 3.5 and ratios of 1 or 2; but with quebracho it was necessary to raise the pH to 4.0 before any extensive precipitation occurred. The addition of 1.5 or 3 equivalents acetate per atom of chromium had no obvious effect on precipitation, but citrate in corresponding amounts completely prevented the precipitation of tannic acid; only a slight precipitate was formed with mimosa and quebracho, and with myrobalans precipitation was greatly reduced.

A similar series of solutions was adjusted to pH 4.0 and heated at 100°C. for 3 hours. The pH fell to 3.0 or below, and the solutions darkened in color, especially at the higher chromium concentrations. Some precipitate was formed in spite of the low pH, but its appearance differed somewhat from that formed in the cold, tending to be more gelatinous.

These observations establish that interaction between chromium and vegetable tan occurs if the pH and chromium concentration are sufficiently high. The tans can apparently replace acetate from the chromium complex but not the more strongly complexing citrate anion. Owing to the difficulties of filtering and washing the precipitates, the possibilities of obtaining any quantitative assessment of the extent to which interaction occurred and the composition of the complexes appeared remote. The darkening of the solutions suggested that some interaction occurred at lower pH without precipitation. This could be due to accelerated oxidation of the tan in the presence of chromium, but the colors of the solutions were different from those of the corresponding tan solutions heated alone at higher pH values.

It was, therefore, decided to see whether further information could be obtained from spectrophotometric measurements.

II. Measurements of Absorption Spectra

Tannic acid solutions were refluxed with chromic sulfate or nitrate solutions, and the optical density was determined over the range 400–700 m μ . In all cases the concentration of chromium was 0.14%, and the tannic acid concentration was varied between 0.5% and 16%. The solutions were adjusted to pH 2.0 before mixing to reduce complications due to precipitation and fell to about 1.4 during refluxing. Under these conditions little or no precipitate was formed except when the time of heating was prolonged.

The absorption curves obtained with a series of chromic nitrate–tannic acid solutions refluxed for 2 hours are shown in Fig. 1. A similar series of curves were obtained with chromic sulfate, but the absorptions were lower at all wavelengths.

51-Chromium was located by autoradiography, using Ilford Industrial G plates, or by direct scintillation counting of areas cut out from the chromatograms.

A limited number of separations were carried out on 2 x 90 cm. columns of Solka Floc B. W. 200. This material was purified by washing successively with 25% HCl, water, acetone, and finally water again. The columns were equilibrated and eluted with 0.01N Na₂SO₄ adjusted to pH 2.5 with H₂SO₄. Three ml. fractions were collected and diluted 1 in 100 for scintillation counting.

Analyses.—Total solids and tan were determined by the S.L.T.C. Official Methods (14). Chromium was determined by perchlorate oxidation and titration with ferrous ammonium sulfate (15).

Oxygen absorption.—The uptake of oxygen by the tanning extracts was determined using a constant volume Warburg apparatus. Three ml. tanning solution (10% W/V with respect to tan) was placed in the flask, and 1 ml. chromic sulfate solution (or water) was added to give final concentrations of 0%, 0.2%, and 2.0% Cr₂O₃ (0%, 0.14%, and 1.4% Cr). Each solution was initially adjusted to pH 2.0. The decrease in pressure at constant volume was measured over periods of up to 100 hours at 30°C., and the uptake of oxygen was calculated and expressed in terms of moles oxygen per 10⁵ g. tan.

RESULTS

I. Precipitation of Vegetable Tannins by Chromic Sulfate Solutions

Some preliminary tests were carried out on the effect of additions of increasing amounts of a chromic sulfate solution to solutions of tannic acid, myrobalans, mimosa, and sulfited quebracho containing 10 g. tan per 100 ml.

All solutions were adjusted to pH 2.0, and chromic sulfate was added to give 0.015, 0.03, 0.06, 0.12, and 0.24 g. Cr per g. tan or, assuming an average molecular weight of 1700 for the tans, molar ratios of Cr/tan of 0.05, 1.0, 2.0, 4.0, and 8.0.

The pH was adjusted to 4.0 with sodium hydroxide, and the solutions were left to stand overnight. The pH fell in all cases to 3.5 or less, and the solutions darkened in color. With tannic acid, myrobalans, and mimosa a heavy precipitate was formed; with the first two, precipitation increased with the chromium concentration, but with mimosa, maximum precipitation occurred with ratios of one or two to one. Little precipitate formed with quebracho, but the solutions became increasingly darker brown in color as the chromium concentration was raised.

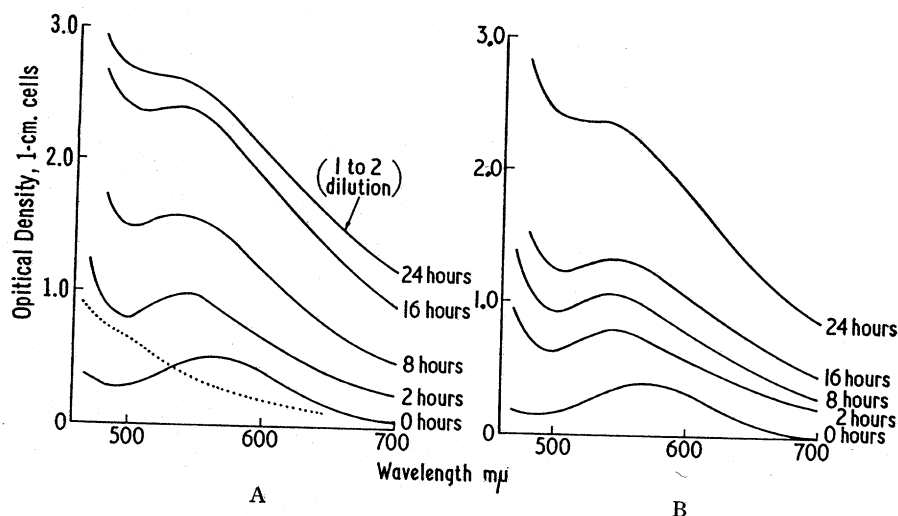


FIGURE 2.—Absorption curves of tannic acid-chromium nitrate (A) and chromium sulfate (B). 0.14 g. Cr refluxed with 3.2 g. tannic acid in 100 ml. for various times. Dotted line gives curve for tannic acid heated alone for 24 hours.

The maxima and minima gradually became less marked during heating and were eventually almost indistinguishable from the general over-all increase.

Experiments have also been carried out with mimosa and quebracho, but with myrobalans this was impossible owing to the cloudiness of the solutions and the readiness with which precipitation occurred. Nontans as well as tans are involved, but as the primary object of the investigation was to gain information on the relative effects of the two materials in retanning, they were compared on a tan basis. Amounts of extract corresponding to 2.55, 4.5, or 9.0 g. tan were heated with 0.14 g. chromium as chromic sulfate in 100 ml. solution in closed bottles for 8, 16, and 24 hours. These amounts correspond to 1.5, 3, and 6 g. Cr per 100 g. tan, or on the basis of a molecular weight of 1700 for the tan, to molar ratios of Cr/tan of approximately 0.5, 1, and 2. Total solids corresponding to these concentrations of tan are indicated in Table I. With tannic acid and mimosa, precipitation began to occur after 16 hours, especially with the lower tan contents, and after 24 hours the experiments were discontinued, but with quebracho there was little precipitation even after 48 hours. In spite of the precipitation, absorption continued to increase over 24 hours, but comparisons are best based on values obtained after 8 hours (Fig. 3 and Table I). Except with the tannic acid the contribution of the chromium to the absorption is small, and the increases must be attributed to changes in the tan. The results in Table I have, therefore, been expressed in terms of $E_{1\text{cm.}}^{1\% \text{ Tan}}$ or E-value, i.e., the absorption of a 1% solution of tan in a 1-cm. cell, the probable contribution of the chromium being

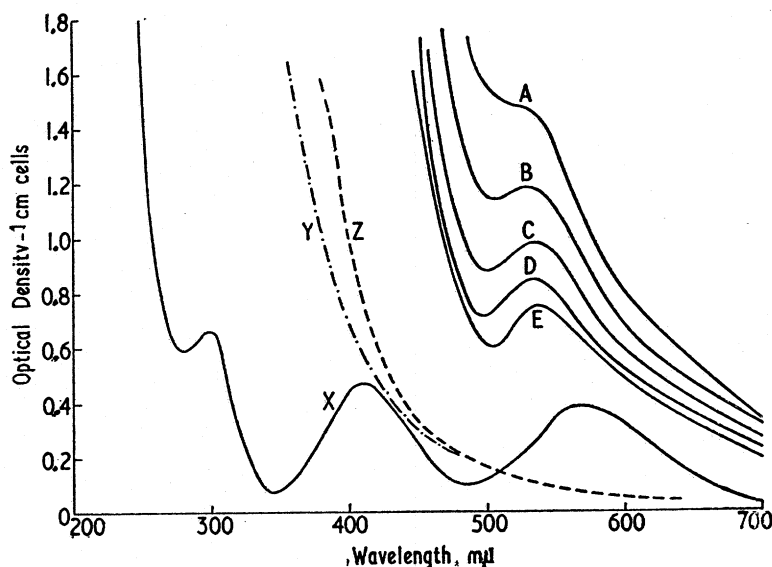


FIGURE 1.—Absorption curves of tannic acid-chromium nitrate solutions after refluxing for 2 hours. Solution containing 0.14 g. Cr per 100 ml. refluxed with various amounts of tannic acid.

A	56 g. tannic acid per g. Cr	
B	28 g. " " " "	
C	14 g. " " " "	
D	7 g. " " " "	
E	3.5 g. " " " "	
X	Chromium nitrate alone	
Y	3.2% tannic acid unheated	} concentrations equivalent to Curve B
Z	3.2% " " heated	

The absorption of tannic acid increases slightly on heating alone (Fig. 1 - curves Y and Z), but in the presence of chromium the increases are much greater. The chromium absorption peak at 570 mμ is apparently shifted to shorter wavelengths; it does not, however, increase in relation to the rest of the curve but tends to merge into the general over-all increase as the tannic acid concentration is increased. It seems probable, therefore, that the increases in optical density observed are mainly due to changes in the tannic acid absorption due either to complex formation or to accelerated oxidation.

The effect of time of heating is illustrated in Fig. 2, which shows the absorption curves obtained when solutions of tannic acid were refluxed with chromic sulfate and nitrate solutions to which 2% of the corresponding sodium salts had been added. Although the presence of salts decreased the changes in absorption, it reduced variations in pH and the tendency for precipitation on longer times of heating.

Absorption continued to increase over periods of 48 hours; at this point precipitation began to be appreciable, and the experiment was discontinued.

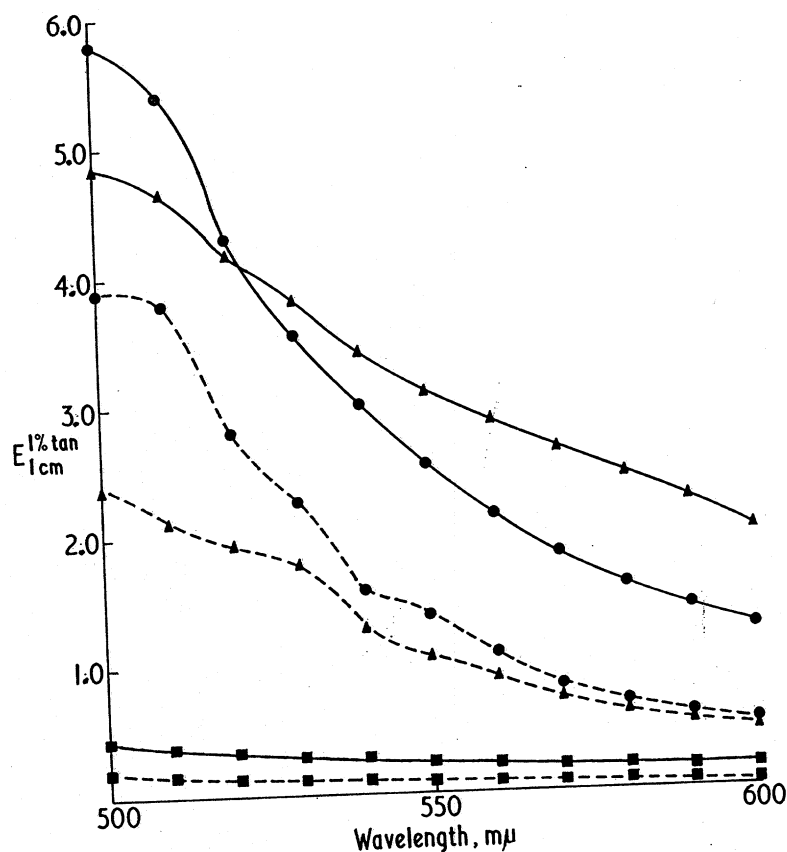


FIGURE 3.—Absorption curves of tannic acid, mimosa, and quebracho heated for 8 hours at 100°C. with and without added chromium sulfate— $E_{1\text{ cm}}^{1\% \text{ tan}}$.

10 g. tan and 0.14 g. Cr per 100 ml.

■ — ■ tannic acid
● — ● quebracho
▲ — ▲ mimosa

(broken lines without added Cr)

subtracted. With all three materials the E-value increases with the ratio of Cr/tan, but with quebracho the increase is relatively small.

Since this experiment showed that the increases in absorption were primarily due to changes in the tan, further tests were carried out in which measurements were extended to cover the absorption peaks characteristic of phenolic compounds. Simpler phenolic compounds such as catechol, pyrogallol, and resorcinol were also included, and more dilute solutions of "tan" were used to minimize precipitation. Chromic sulfate (= to 0.21 g. or 4 millimoles

TABLE I

$$E \frac{1\% \text{ tan}}{1 \text{ cm.}} \text{ at } 540 \text{ m}\mu$$

g. Cr per 100 g. "tan"	Tannic Acid			Mimosa			Quebracho		
	8 h.	16 h.	24 h.	8 h.	16 h.	24 h.*	8 h.	16 h.	24 h.
0	0.112	0.140	0.149	1.28	2.05	2.22	1.79	2.15	2.15
1.5	0.275	0.286	0.396	2.87	5.50	4.16	2.91	4.50	5.78
3.0	0.325	0.380	0.743	3.46	6.98	7.25	3.03	6.08	7.73
6	0.490	0.545	0.711	5.84	9.83	11.46	3.54	6.16	7.78
Nontans per 100 g. tan	10.2			42.3			22.6		

*Extensive precipitation.

TABLE II

ABSORPTION OF TANS AND OTHER PHENOLIC COMPOUNDS AFTER
HEATING WITH AND WITHOUT CHROMIC SULFATE FOR 24 HOURS

$$E \frac{1\% \text{ tan}}{1 \text{ cm.}}$$

Wavelength	As Made Up	Heated Alone	Heated with Chromic Sulfate*
<i>Catechol</i>			
275 mμ—maximum	213	210	270
420 mμ	0.01	0.68	2.53
<i>Pyrogallol</i>			
267 mμ—maximum	54	66	114
420 mμ	0.01	1.7	8.3
<i>Resorcinol</i>			
275 mμ—maximum	160	162	162
420 mμ	0.02	0.30	0.19
<i>Tannic acid</i>			
275 mμ—maximum	404	441	440
420 mμ	0.21	0.98	4.5
<i>Mimosa</i>			
280 mμ—maximum	195	162	196
420 mμ	2.31	4.03	27.6
<i>S. quebracho</i>			
280 mμ—maximum	336	293	278
420 mμ	2.8	7.3	30.4

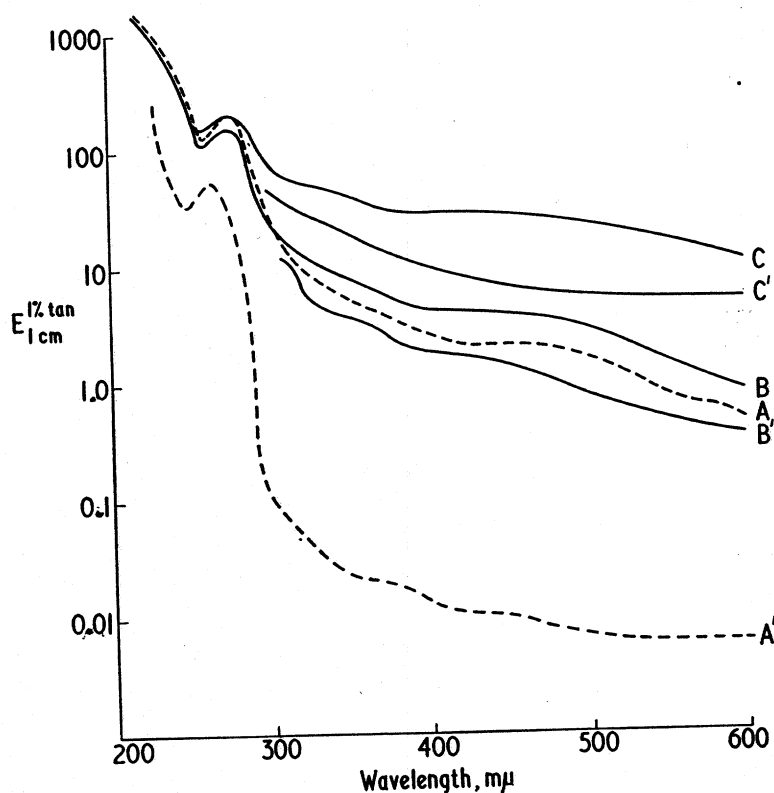


FIGURE 5.—Absorption curves of mimosa (1.16 g. tan per 100 ml.) and pyrogallol (0.5 g. tan per 100 ml.) heated for 24 hours with and without the addition of chromium sulfate—E $\frac{1\% \text{ tan}}{1 \text{ cm.}}$

- A—Mimosa unheated
- B—Mimosa heated
- C—Mimosa heated with chromium—0.105 g. Cr per 100 ml. or 1 mole Cr per equivalent of tan
- A', B', and C'—corresponding curves for pyrogallol

The increased absorption in the presence of chromium could be due to accelerated oxidation of the tan. Comparison of solutions heated in closed vessels in nitrogen with those heated under reflux showed that exclusion of oxygen slightly reduced the increases in absorption observed when the tans were heated alone but had little effect on the increases observed in the presence of chromium. Changes in absorption spectra are, therefore, presumably due mainly to complex formation, although accelerated oxidation probably plays some part.

Cr) was heated with 4 milliequivalents of tan in 100 ml. solution for 24 hours at 100°C. For this purpose the equivalent weight of tannic acid was taken as 170, i.e., the unit containing 1 mole of gallic acid and that of the other compounds as the unit containing two hydroxyl groups ortho to one another, i.e., approximating to catechin, molecular weight 290. Typical absorption curves are shown in Figs. 4, 5, and 6.

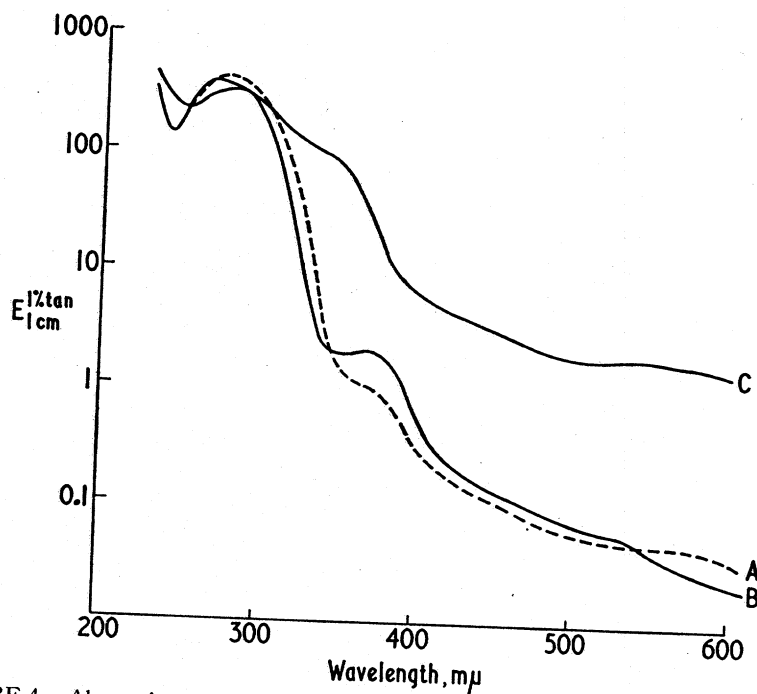


FIGURE 4.—Absorption curves of tannic acid (0.68 g. tan per 100 ml.) heated with an amount of chromium sulfate for 24 hours—E $\frac{1\% \text{ tan}}{1 \text{ cm.}}$

- A—Tannic acid alone
- B—Tannic acid heated
- C—Tannic acid heated with 0.105 g. Cr per 100 ml. or one mole Cr per equivalent of tan

The strong benzenoid absorptions at about 200 and 270 $m\mu$ shown by all the compounds were little affected by heating. With pyrogallol, catechol, and tannic acid there were slight increases in the presence of chromium but not with mimosa, quebracho, or resorcinol. At longer wavelength, increases in absorption were much greater, particularly in the presence of chromium. With resorcinol the increases on heating alone were much less than with the other compounds, and there was no evidence that the presence of chromium caused any additional increase. In all cases the absorption continued to increase over long periods of time at room temperature.

at the origin, while in the last two solvents essentially all the chromium migrated with the solvent front, leaving only a small fraction at the origin and, with the 0.001*N* H₂SO₄, a little distributed along the chromatogram. There was no evidence that the migration of the chromium was affected by the presence of the three phenolic compounds (catechol, pyrogallol, and resorcinol) or of tannic acid. The distribution of the phenolic compounds, with the exception of resorcinol, was changed by heating, and these changes were accentuated in the presence of chromium. In the main the changes were in the direction of decreased migration, and in particular, the amount of material remaining at the origin was increased in the presence of chromium. With tannic acid the spot identified as gallic acid was increased by heating but was little affected by the presence of chromium.

A few two-dimensional chromatograms were run on No. 2 paper using either 10% acetic acid followed by butanol-acetic acid-water (63:10:27) (16) or butanol-0.1*N* sulfuric acid (5:1) followed by benzyl alcohol-tertiary butanol-secondary propanol-water (3:1:1:1) containing 1.8% w/v formic acid (17). Again there was little indication that the migration of the chromium was affected by the tans. With tannic acid, heating led to the formation of gallic acid and a number of new spots appeared; in the presence of chromium these spots were intensified, and an appreciable amount of material remained at the origin. Mimosa and quebracho were relatively little affected by heating alone, but in the presence of chromium several new spots appeared, and migration was, in general, reduced. Spots showing fluorescence under ultraviolet light were greatly reduced.

A 4% solution of tannic acid containing 0.07% ⁵¹Cr as chromic sulfate was heated in a sealed tube at 100° for 48 hours and chromatographed on a column of Solka Floc 2 x 90 cm. On development with 0.01*N* Na₂SO₄ at pH 2.5, five distinct bands brown in color and, therefore, presumably containing tannic acid could be seen having *R* values (18) of 0.1, 0.5, 0.66, 1.0, and 1.3. Scintillation counting of the eluted fractions showed that chromium was present in all these bands and more particularly in the two fastest (65% and 20% of the total chromium).

Similar catechol-chromic sulfate solutions separated into four bands; the two fastest were blue in color, the third was yellow, and the fourth, very slow moving, was dark blue. The chromium was distributed approximately equally among the three blue bands. Chromic sulfate under corresponding conditions ran as a single green band with *R* approximately 2.0. Thus, although the fastest moving band in each case may represent uncomplexed chromium running with tannic acid or catechol, there is evidence for the presence of four tannic acid-chromium complexes and three catechol-chromium complexes, involving up to 35% and about 60% of the total chromium, respectively. Failure to detect the presence of such complexes on paper chromatograms may be due to the much lower concentration of tannic acid

Paper chromatography, however, showed clearly that the presence of chromium greatly accentuated the changes in the tan occurring as a result of heating. Since it also increased absorption of oxygen, these changes are presumably oxidative and lead to polymerization and hence reduced solubility in the developing solvents.

The balance of evidence, therefore, suggests that under favorable conditions appreciable complex formation can occur between chromium and the constituents of vegetable tanning extracts, and that, in addition, chromium accelerates the oxidation of vegetable tannins. With the tans the readiness with which precipitation occurs suggests that complex formation with the tan as opposed to nontans decreases in the order myrobalans > mimosa > sulfited quebracho. The fact that citrate completely prevented precipitation while acetate had little effect indicates that the complexing affinity of the vegetable tans lies somewhere between the two. Acetate is relatively inefficient with respect to the extraction of chromium from leather, while citrate is one of the most effective anions. The spectrophotometric evidence also suggests that mimosa complexes more readily than quebracho. The number of different complexes formed is probably high, and any attempt to isolate and characterize these would hardly repay the effort involved.

Judging from the amounts of oxygen taken up, of the four materials tested, mimosa is by far the most susceptible to oxidation, and myrobalans the least. Of the three simple phenolic compounds examined, pyrogallol appears to be the most susceptible to oxidation, but the changes occurring in the presence of chromium are less than with catechol, suggesting that complex formation is greater with the latter. The relatively small changes occurring with resorcinol suggest that the presence of two hydroxyl groups ortho or para to one another is necessary for both oxidative changes and complex formation. On the basis of conductometric measurements Shuttleworth (19) also concluded that pyrogallol and catechol formed complexes with chromium, whereas resorcinol did not.

The implication of these findings with respect to combination-tanned leathers containing both chromium and vegetable tans is obvious. If complex formation can occur in a few hours at 100°C., then it is likely to occur slowly at lower temperatures, and provided there is sufficient moisture in the leather, extensive interaction could occur. This provides strong support for the hypothesis put forward earlier (1) regarding the reasons for the poor resistance of vegetable-chrome combination-tanned leathers to moist heat. First, the leather will become more acid due to the displacement of sulfate ions from the chrome complex, and second, detannage will occur owing to the displacement of protein carboxyl groups, both of these increasing the likelihood of hydrolytic breakdown of the protein fibers. Although the present experiments indicate that interaction is favored by rise in pH, this will probably not be of significance in practice. It is the increased acidity coupled with detannage which will be the more important factor governing deterioration.

Of the three tanning materials tested, quebracho appears to be the least likely to displace sulfate or protein carboxyl groups from the chromium complex. All that can be said about the amounts of vegetable tan required for optimum stability is that the higher the concentration of vegetable tan the greater will be the detannage, while in order to obtain maximum resistance to perspiration it is necessary to have about half a mole of vegetable tan for every chromium complex (12), i.e., on the basis of 2 chromium atoms per complex, 4 parts vegetable tan for every part Cr_2O_3 .

The implications of the increased oxidation of vegetable tan occurring in the presence of chromium are difficult to assess. The increase in pH value due to the absorption of perspiration will accelerate oxidation, but the fact that chromium will tend to precipitate the vegetable tan under these conditions may result in a decrease rather than an increase in oxidation.

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